

# Mössbauer Diagnostics of the Isomorphic Substitution of Iron for Aluminum in Triclinic Iron Vanadate

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**Abstract**—Mössbauer spectroscopy and X-ray powder diffractometry (XRD) phase analysis are used to study mixed vanadates with the composition  $\text{Al}_x\text{Fe}_{3-x}\text{V}_3\text{O}_{12}$ , where  $x$  is 0, 0.3, 1.0, 1.5, 2.0, 2.7, and 3.0. Mössbauer spectroscopy is used to study the distribution of trivalent cations over different crystallographic positions. It is shown that the distribution of aluminum atoms differs from those expected from statistic and thermodynamic models.

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## INTRODUCTION

Materials based on iron and vanadium compounds, which include material doped by transition or non-transition metals, are widely used as catalysts [1, 2] and sensor materials [3]. Apart from solid solutions, two individual compounds form in the iron(III) oxide–vanadium(V) oxide system in particular:  $\text{Fe}_2\text{V}_4\text{O}_{13}$  and  $\text{FeVO}_4$  [6]. In turn, iron ortovanadate  $\text{FeVO}_4$  crystallizes depending on the conditions in an orthorhombic [7] or triclinic [8] system. In addition to its use in catalysis, triclinic iron vanadate has recently attracted attention due to its interesting magnetic properties. The type of iron vanadate formed at normal pressures is a multiferroic [9], and antiferromagnetic ordering is observed in it at temperatures below 22 K [10].

The special magnetic properties of triclinic iron vanadate are determined by its structural properties. It is known that in the crystal lattice of triclinic iron vanadate  $\text{FeVO}_4$ , both iron and vanadium atoms occupy three nonequal crystallographic positions [8]. The different positions of vanadium and iron atoms determine the different neighboring atoms. If in the case of vanadium changes in the oxygen environment are only minor (the vanadium–oxygen distances change but the tetrahedral motive is preserved [11]), in the case of iron the changes are greater. Two iron atoms are thus located in differently distorted octahedral polyhedrons. The sizes of the voids in oxygen octahedrons differ: for one atom, the iron–oxygen distances can vary from 1.936 to 2.102 Å; for another, they can vary from 1.960 to 2.045 Å. The third iron atom is inside a severely distorted trigonal bipyramid with iron–oxygen distances of 1.869 to 2.019 Å. Three pairs of the described iron-containing polyhedrons are connected in tandem along their edges in S-shaped planar fragments that contain six iron atoms each. In the crystal

lattice, the latter are arranged in layers and connected in between by vanadium containing tetrahedrons [8]. Considering the above description of the compound's structure, the properties of iron vanadate should be described more precisely by the formula  $\text{Fe}_3\text{V}_3\text{O}_{12}$ .

This is confirmed by Mössbauer spectra, in which three doublets are found [8] in different crystallographic positions. The doublet with great quadrupole splitting corresponds to the iron atoms in a trigonal bipyramid [8], while the two doublets with smaller quadrupole splitting and similar isomeric shifts are associated with the iron atoms in the voids of an octahedron.

This work examines the Mössbauer spectroscopy of products from replacing iron atoms in triclinic vanadate with aluminum atoms in order to find the distribution order of trivalent cations over different crystallographic positions, and to relate the doublet parameters of iron atoms in the indicated positions.

## EXPERIMENTAL

Aluminum oxide of analytical grade, preliminary baked in air at a temperature of 1000°C for 10 h, iron (III) oxide of reagent grade, and vanadium (V) oxide of analytical grade were used as our initial compounds. The samples were synthesized using the standard methods of solid synthesis. To prepare the samples, these oxide mixtures were mixed in the required ratio, ground in a corundum mortar, pressed into tablets 8 mm in diameter and 1–2 mm in height, put in the initial charge in an alumina vessel, and annealed in air for 50–70 h at a temperature of 650°C. After cooling, the tablets were ground again and compressed and annealed as described above, but at a temperature of 675°C. After repeated annealing and grinding, the samples were powders ranging from light to dark

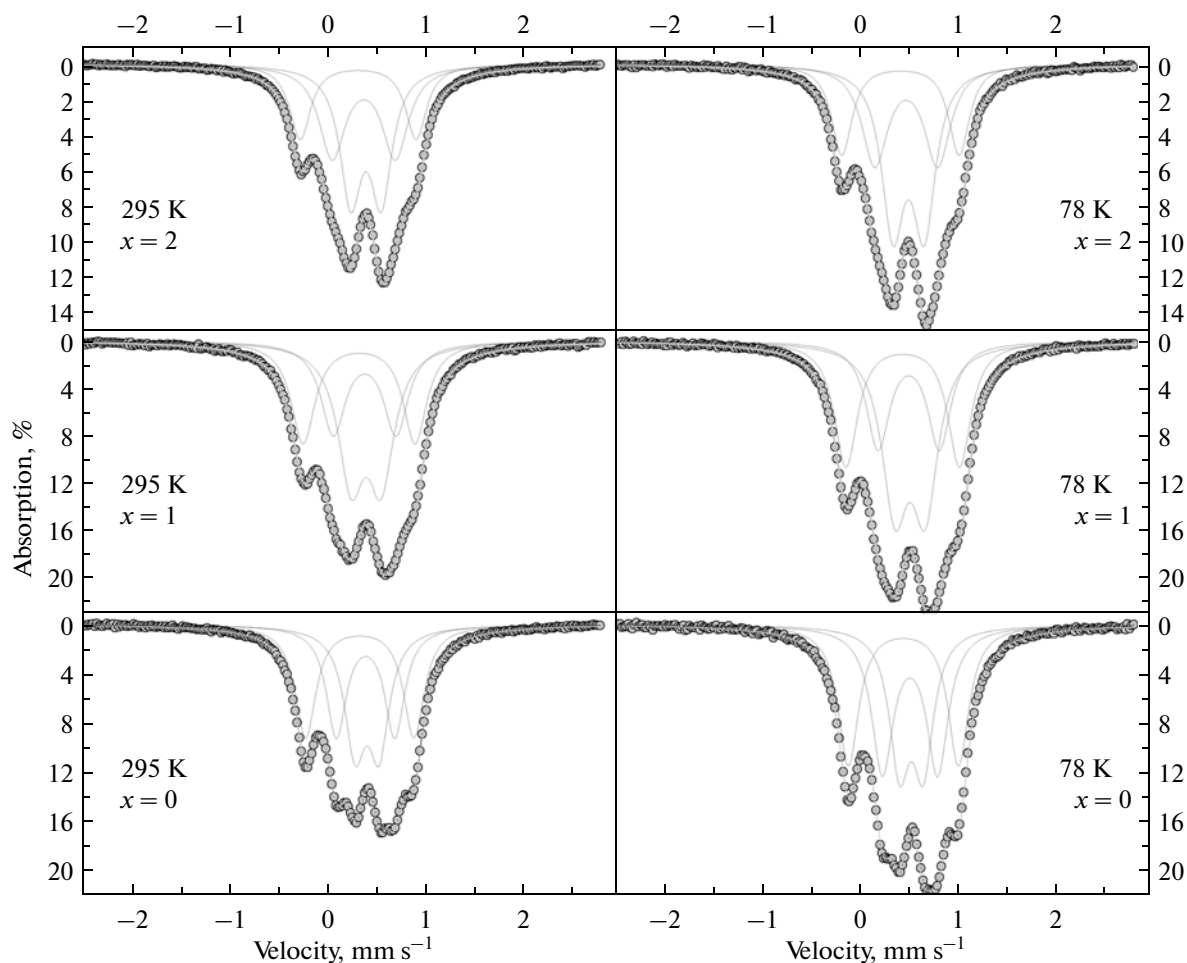


Fig. 1. Mössbauer spectra of some ortovnadates with  $\text{Al}_x\text{Fe}_{3-x}\text{V}_3\text{O}_{12}$  composition at different temperatures.

brown, depending on content. The samples were stable in a dry atmosphere for at least one year.

The X-ray diffraction data in the range  $2\Theta$  of 5 to 80 degrees were obtained on a D/Max-2500 diffractometer (Rigaku Corporation, Japan) equipped with a graphite monochromator and using  $\text{CuK}\alpha$  irradiation ( $\lambda = 0.15418$  nm).

Mössbauer absorption spectra were recorded on an MS1104EM Mössbauer express spectrometer (ZAO Kordon, Rostov-on-Don). Our Mössbauer sources of  $\gamma$  radiation (ZAO RITVERTs, St. Petersburg) contained  $^{57}\text{Co}$  in a metal rhodium matrix with activities of 3 and 35  $\mu\text{K}$ . To obtain the spectra, the powder samples were placed in a plastic cell and placed in a vacuumed cryostat. The spectra were recorded at room temperature and the nitrogen boiling temperature with a quality of no less than 100 for a resolution of 1024 points for each sample. The error in thermostating the samples was  $\pm 1$  at the nitrogen boiling temperature and  $\pm 4$  at room temperature. The reproducibility of the spectra was controlled by comparing the spectra obtained at room temperature for a sample before and after vacuum treatment and after a

cooling–heating cycle. Mathematical processing of experimental Mössbauer spectra was done for the high-resolution spectra (1024 points) using the Univem MS 9.08 program. The spectra were described by a combination of symmetric doublets. Values of the chemical shifts in this work are considered with respect to  $\alpha\text{-Fe}$ .

## RESULTS AND DISCUSSION

The crystal lattices of iron and aluminum ortovandates [8, 12] are of one structural type:  $\text{ZnMoO}_4$ . These structures belong to P1 point group of triclinic symmetry and contain 18 nonequivalent atoms of the elements in a unit cell. After the application of symmetry operations, the number of atoms in the unit cell grows to 36, corresponding to formula units  $\text{MVO}_4$  [13]. Considering the difference between the crystal-chemical radii of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions, the difference between the structures of iron and aluminum are reduced to the difference between unit cell parameters, increasing the volume of the iron-containing cell by 8.4% with respect to an aluminum-containing cell. It is therefore obvious that these compounds form a

**Table 1.** Parameters of the Mössbauer spectra of  $\text{Al}_x\text{Fe}_{3-x}\text{V}_3\text{O}_{12}$  ortovanadate and the fraction of substituted Al atoms in respective crystallographic positions  $n_i$ 

Temperature, K		295						78					
$x$	Subspectrum <sup>1</sup>	$\delta$	$\Delta$	$\Gamma_{exp}$	$S, \%$	$\chi^2$	$n_i$	$\delta$	$\Delta$	$\Gamma_{exp}$	$S, \%$	$\chi^2$	$n_i$
		mm s <sup>-1</sup>						mm s <sup>-1</sup>					
0.0	D2	0.32	1.11	0.26	34	1.01	0	0.43	1.13	0.26	34	1.02	0
	D3	0.38	0.59	0.25	33		0	0.49	0.56	0.27	33		0
	D1	0.40	0.24	0.25	33		0	0.51	0.24	0.25	33		0
0.3	D2	0.32	1.12	0.29	35	1.23	0.11	0.42	1.13	0.28	35	1.50	0.06
	D3	0.38	0.60	0.29	32		0.13	0.48	0.59	0.27	28		0.23
	D1	0.39	0.26	0.30	33		0.06	0.49	0.27	0.31	37		0.01
1.0	D2	0.32	1.15	0.29	30	1.08	0.40	0.42	1.16	0.29	31	1.49	0.38
	D3	0.37	0.64	0.30	28		0.45	0.48	0.63	0.29	26		0.48
	D1	0.39	0.31	0.32	42		0.15	0.49	0.31	0.32	43		0.14
1.5	D2	0.31	1.16	0.28	26	1.04	0.61	0.42	1.18	0.27	27	1.19	0.59
	D3	0.37	0.63	0.34	35		0.47	0.48	0.63	0.29	28		0.58
	D1	0.39	0.31	0.30	39		0.40	0.50	0.32	0.30	45		0.33
2.0	D2	0.31	1.18	0.25	23	1.52	0.77	0.40	1.20	0.26	24	1.17	0.76
	D3	0.36	0.64	0.33	37		0.63	0.46	0.64	0.32	32		0.68
	D1	0.39	0.32	0.27	40		0.59	0.48	0.32	0.28	44		0.56
2.7	D2	0.30	1.21	0.29	22	1.06	0.93	0.41	1.22	0.28	23	1.08	0.93
	D3	0.36	0.66	0.36	32		0.91	0.47	0.65	0.32	28		0.92
	D1	0.38	0.32	0.29	46		0.86	0.49	0.32	0.29	49		0.85

Note: (1) The symbol for the subspectrum coincides with the symbols used in the text for crystallographic positions.

continuous series of solid solutions with a relatively uniform distribution of trivalent cations over different unit cells.

This assumption is confirmed by X-ray powder diffraction for the samples tested in this work. It follows from the XRD data that the products formed using our technique are single-phase and isostructural. In addition, there were no reflections of the initial components or other products of interaction in the diffraction patterns of the investigated products.

The Mössbauer spectra of unsubstituted triclinic iron vanadate at room temperature and the temperature of liquid nitrogen were superpositions of three doublets (Fig. 1). One of these (D2, Table 1) differed considerably in its parameters of the isomeric shift and quadrupole splitting from the other pair of doublets. The D2 doublet is probably associated with the iron atoms in the polyhedron of the trigonal bipyramid, while other two are associated with the iron atoms in the octahedral environment. The same temperature dependence of the isomeric shift is observed for all doublets. Specific features of the spectra of triclinic

iron ortovardanate are the narrow lines of each doublet and their close values.

The Mössbauer spectra of the ortovardanates of iron replaced with aluminum differ from the spectra of the unsubstituted compound, especially in their worse resolution of internal doublets. These spectra can nevertheless be adequately described via the superposition of three doublets (Table 1), for which the parameters of unsubstituted iron vanadate can be used as an initial approximation.

Let us analyze the change in parameters of Mössbauer spectra for ortovanadates of  $\text{Al}_x\text{Fe}_{3-x}\text{V}_3\text{O}_{12}$  composition upon an increase in the  $x$  parameter (Table 1). Partial replacement of iron atoms with aluminum initially leads to a minor change in the isomeric shifts for each doublet. A greater change leading to a reduction in the isomeric shifts is observed for compositions with  $x > 1.5$ . This value of the quadrupole splitting of the doublet corresponding to the respective iron atom in the trigonal–bipyramidal polyhedron increases monotonically with an increase in the  $x$  parameter. If a doublet with average quadru-

**Table 2.** Variants of the distribution of aluminum and iron atoms in  $\text{Al}_2\text{Fe}_4$  hexa nuclear clusters

Variants of distributions	Designation of the crystallographic position					
	I	II	III	III	II	I
1	Al	Al	1	0	0	0
2	1	Al	Al	1	0	0
3	Al	2	Al	1	0	0
4	0	1	Al	Al	1	0
5	1	Al	2	Al	1	0
6	Al	1	1	Al	1	0
7	0	0	1	Al	Al	1
8	0	1	Al	2	Al	1
9	1	Al	1	1	Al	1
10	Al	1	0	1	Al	1
11	0	0	0	1	Al	Al
12	0	0	1	Al	2	Al
13	0	1	Al	1	1	Al
14	1	Al	1	0	1	Al
15	Al	1	0	0	1	Al

Note: Designation Al: The position is occupied by an aluminum atom;

Number: The position is occupied by an iron atom;

2: The iron atom is connected to two aluminum atoms;

1: The iron atom is connected to one aluminum atom;

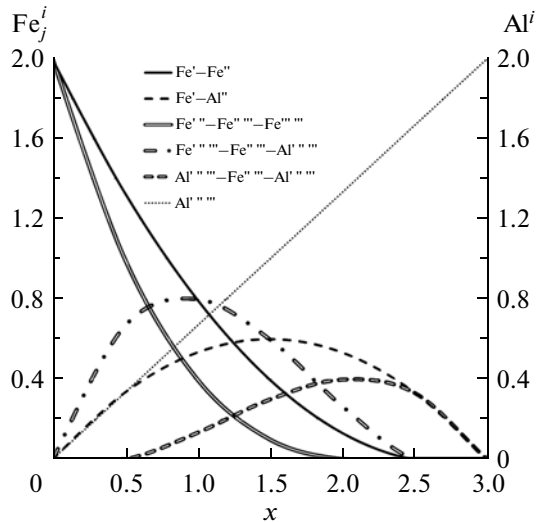
0: The iron atom has an ordinary environment, as in nonsubstituted iron ortovanadate.

pole value is considered, there is a gap in the  $\Delta(x)$  function at  $x$  from 1 to 1.5, while the quadrupole value increases as a whole. Quadrupole splitting for a doublet with a minimum quadrupole increases in the range of  $x = 0-1$ , and then remains virtually unchanged. The width of the resonance lines for two doublets with minimum and maximum values of quadrupole splitting changes symbatically: they grow in the range of  $x = 0-1$ ; from 1 to 2, they diminish and then grow again. The width of the resonance line in a doublet with the average quadrupole grows over almost the entire range of  $x$  values. In addition, the doublet with the average quadrupole value has wider lines than the other doublets. The described changes in Mössbauer parameters depend on the sample composition, but are virtually independent of the temperature at which the spectra are recorded.

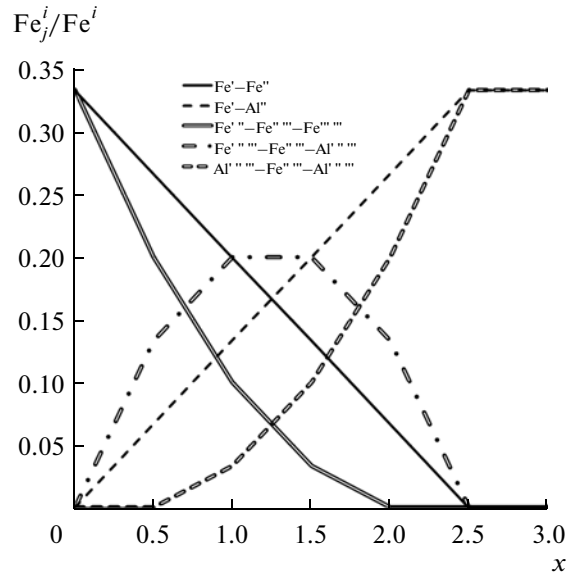
The observed changes in the parameters of Mössbauer spectra are obviously associated with the change in relative content of aluminum atoms in the samples. Since the Mössbauer parameters are associated with the environment of the iron atoms, a change in them

indicates the transformation of the environment. In order to describe the changes in the environment of iron atoms in substituted triclinic vanadate, let us consider a simplified statistical model. As was mentioned above, hexa nuclear linear S-shaped fragments can be distinguished in the structure of triclinic iron vanadate. The metal atoms on the ends of these clusters (the first and sixth positions) occupy a void in an octahedral polyhedron consisting of oxygen atoms. The atoms in the second and in fifth positions are in a trigonal-bipyramidal environment. The atoms in the third and the fourth positions are in an octahedral environment. A second-fold axis can be drawn down the center of these fragments (between the third and the fourth metal atoms), so we can designate the metal atoms' positions as I-II-III-III-II-I. At  $x = 0$ , all positions are filled with iron atoms; at  $x = 3$ , with aluminum atoms. At intermediate values of  $x$ , under the condition of a uniform distribution of different kinds of atoms in crystallites, some positions in the clusters will be occupied by either iron atoms or aluminum atoms. For the sake of precision, we shall consider the case of replacing iron atoms with aluminum atoms. On the whole, the distribution of doping aluminum atoms in the hexa nuclear clusters can be statistical. However, substituting an aluminum atom for any iron atom will produce changes as a consequence of the bonds between iron containing polyhedrons (i.e., distortions in their environment) and thus affect the changes in respective Mössbauer parameters. For the sake of simplicity, let us consider three variants of an iron atom environment: First, an iron atom is in an ordinary environment. For an atom in position I, this means contact with one iron atom, while atoms in positions II and III (identified in the figures as  $\text{Fe}''$  and  $\text{Fe}'''$ ) are in contact with two iron atoms each. The second variant is an iron atom joined with one foreign aluminum atom. For iron atoms in position I, there is only one possibility, Al'', while for atoms in positions II and III, there are two possible distributions. The third variant is possible only for iron atoms in the second and the third positions, when an atom is joined with to two foreign metal atoms. The variant in which aluminum atoms replace iron atoms in this position leads to a loss of resonance, and affects only the respective doublet area in the Mössbauer spectra (see below).

The probability of observing one variant or another of a change in the environment of iron atoms in each position of substituted vanadate depending on the fraction of substitution  $x$  can be easily calculated. Let us consider, e.g., the case  $x = 1$ , which corresponds to cluster of  $\text{Al}_2\text{Fe}_4$  (Table 2). As can be seen from Table 2, only 15 variants of the distribution of two aluminum atoms and four iron atoms over six positions in a linear cluster are possible. In twelve out of fifteen variants, the environment of the iron atom in position I does not change. In eight cases, there is contact with an aluminum containing polyhedron, while in ten cases the



**Fig. 2.** Dependence of the number of iron  $Fe_j^i$  and aluminum  $Al^i$  atoms in the  $i$ -th position and in respective environment  $j$  on the degree of substituting  $x$  in  $Al_xFe_{3-x}V_3O_{12}$ .



**Fig. 3.** Dependence on the fraction of  $Fe_j^i$  iron atoms in the  $i$ -th position in respective surrounding  $j$  on the degree of substituting  $x$  in  $Al_xFe_{3-x}V_3O_{12}$ .

iron atom in this position is replaced with nonresonance aluminum.

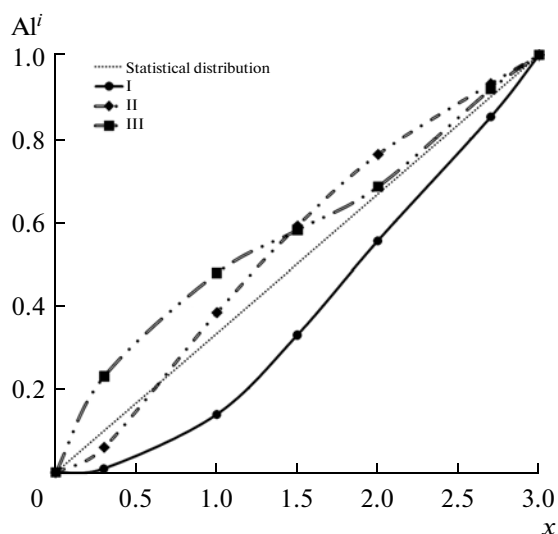
In the same way, we can consider the probabilities of the distribution of the above three variants of the environment for other values of  $x$  that are multiples of 0.5. For intermediate values of  $x$ , the solution is obviously the sum of the probabilities at the nearest points with the respective weight coefficients. From our data, it is easy to calculate the probability of observing each variant of the iron atom environment (see Fig. 2, where the probability is multiplied by 2 and corresponds to the number of atoms in this environment) or the corresponding fraction of iron atoms depending on parameter  $x$  (Fig. 3).

It follows from the obtained dependences that the fractions of atoms in different environments depend in a complicated manner on the degree of substitution. For iron atoms in the end octahedron (position I), the number of atoms bound to an aluminum-containing polyhedron becomes higher than the number of atoms in a normal environment starting from  $x = 1.25$ . For iron atoms in an intermediate octahedron (position III), an effect of neighboring aluminum atoms becomes important only at  $x > 0.7$ , and at  $x > 1.8$  the main fraction is composed of iron atoms surrounded by aluminum atoms. On the whole, the obtained dependences correlate with the character of the described changes in the Mössbauer parameters of the doublets. Even for this simplified model, however, it becomes clear that for a correct description of the experimental spectra for atoms in position I, we should use the model based on two doublets, not one. For atoms in positions II and III, a minimum of three doublets is required. Since vari-

ants  $Fe''-Fe'''-Al'''$  and  $Al''-Fe'''-Fe'''$  are different, models with four doublets are actually required to describe the state of  $Fe''$  and  $Fe'''$  atoms.<sup>1</sup> Since the variation in the states of iron atoms in an octahedral environment is greater in position III than in octahedral position I, and we use one doublet to describe each position, the doublet with broader lines, i.e., with the mean quadrupole value (D3, Table 1), should correspond to  $Fe'''$ .

In considering the statistical model, we examined the assumption that the probability of distributions of different kinds of atoms over different crystallographic voids was the same. Allowing for the difference between the internal volumes of each of the three oxygen polyhedrons, however, we must assume that the real distributions differ from the statistical ones. The energy states of iron atoms in all crystallographic positions should differ considerably. Consequently, under conditions of isomorphic substitution by other types of atoms with different electron structures, the selective replacement of iron atoms takes place only in definite crystallographic positions according to thermodynamic laws. This phenomenon is well studied for compounds with spinel structure, where different types of atoms of transition elements in two octahedral and one tetrahedral voids can be predicted using the crystal field theory [14] and are determined by the energy advantage of stabilizing by a crystal field. When metal atoms are not those of  $d$ -elements, the size factor is of great importance in the distribution of atoms. The ion

<sup>1</sup> This is obviously one reason for the increase in the  $\chi^2$  criterion for the spectra of samples with intermediate values of  $x$  (Table 1).



**Fig. 4.** Concentration of Al atoms in the  $i$ -th crystallographic position in  $\text{Al}_x\text{Fe}_{3-x}\text{V}_3\text{O}_{12}$  at different  $x$ , determined from the data of Mössbauer spectroscopy at 78 K.

radius of aluminum is far smaller than the iron (III) ion's radius, and this difference exceeds condition of 15% that is conventional for isomorphism [15]; we may therefore expect that aluminum atoms for substitution should first of all occupy the small voids of a trigonal bipyramid, position II. The volumes of octahedral voids are close, so a relatively uniform distribution of aluminum atoms can be expected in them.

It is easy to show the correlation between the areas of doublets  $S(D_i)$  registered in Mössbauer spectra and degree of substitution  $x$  with the concentration of aluminum atoms in the  $i$ -th positions  $n_i = 1 - S(D_i)(3 - x)/100$ . The fractions of atoms replaced with aluminum atoms, calculated from the experimental data for different crystallographic positions, are shown in Table 1 and in Fig. 4. It can be seen that the obtained values deviate considerably from the ones expected for the abovementioned statistical and thermodynamic models. Only at  $x > 1$  does the fraction of aluminum atoms in a trigonal–bipyramidal environment exceed the one expected statistically. At  $x < 1.5$ , aluminum atoms are mainly in position III (Fig. 4). Position I in the fringe octahedron is predominantly occupied by iron atoms over the range of parameter  $x$ . Deviations from the distribution expected statistically at  $x < 1.5$  are quite large (Table 1).

## CONCLUSIONS

We have considered the possible correlation between changes in the parameters of Mössbauer spectra caused by the aluminum distribution in  $\text{Al}_x\text{Fe}_{3-x}\text{V}_3\text{O}_{12}$  triclinic ortovanadates at  $x$  0, 0.3, 1.0, 1.5, 2.0, 2.7, and 3.0. It was shown that the distribution of aluminum atoms over different crystallographic positions differs from the one expected from statistical and thermodynamic models. In the hexa nuclear clusters that are the basis of ortovanadate, aluminum atoms are predominantly in the second and third positions, avoiding the end position. The doublets observed in the spectra are associated with iron atoms in different crystallographic positions.

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